Supporting Information

Johnston et al. 10.1073/pnas.0909248106

SI Text

Calculations of global oxygen budgets were performed as follows. We begin by setting the mass of the atmosphere at 5×10^{18} kg and 20% O_2 for modern examples. Central to linking marine fluxes to atmospheric compositions is an appreciation for scale, understanding that today, at 20% P_{O2}, 10,000 times more O_2 resides in the atmosphere than in the ocean (given an average dissolved oxygen content of 300 ppm). That said, calculated changes in O_2 production are viewed in the context of the mass of the atmosphere and not the volume of the ocean (the solubility of O_2 in seawater will scale with P_{O2} and, to a lesser extent, temperature).

For primary productivity calculations, we assumed a formula weight for organic matter (CH_2O, 30 g/mol) and a set stoichiometric relationship between sulfur and carbon for sulfate reduction (2:1). We take total primary production at 4.5×10^{16} g C/year with an export efficiency of 33% (1). Modern OM burial estimates are taken to be 1.6×10^{14} g C/year (2), leading to a burial efficiency of approximately 0.4%. Modern net rates of sulfate reduction are from Turchyn and Schrag (3) and estimated to be 2.62×10^{12} mol C/year, or two times 7.7×10^{12} mol S/year modified by 83% reoxidation. Estimates of Proterozoic sulfate reduction are derived from an average of values presented in Canfield and Farquhar (4), or 1.7×10^{13} mol C/year; a value that is very similar to today before considerations of reoxidation.

We calculated the potential impact of anoxygenic photosynthesis on O_2 budgets (more specifically P_{O2}) by using modern rates of total primary production, modified by the potential contribution (%) from anoxygenic photoautotrophs. For the modern example, this results in a maximum contribution of 0.17%. Using this formulation, and inserting estimates of Proterozoic sulfate reduction, we find a maximum global contribution from anoxygenic photoautotrophs at 1.13%. Both these values can be converted into molar quantities of oxygen, which can be displaced into the atmospheric reservoir, through relating these percent contributions to OM burial. For instance, using modern rates of burial and a potential 0.17% contribution from anoxygenic photosynthesis, O_2 accumulation would be modified by 9.31×10^9 mol O_2/year. Using Proterozoic estimates for percent anoxygenic photoautotrophy and modern OM burial efficiencies, we calculate changes to O_2 production of 6.03×10^{10} mol O_2/year. When this quantity of O_2 is considered in the context of the mass of the atmosphere, changes to P_{O2} can be directly calculated.

In both cases, this represents a theoretical maximum contribution of anoxygenic photosynthesis using modern primary production and burial rates (5). It is likely, however, that Proterozoic primary production was lower due to nutrient limitations, and burial efficiency was potentially much higher as a result of less oxygen in the water column. These changes, when coupled with lower sulfide oxidation rates (that is, more sulfide available for anoxygenic photoautotrophs), would only increase our estimated contributions. As written in the text, this is most simply conceptualized by tracking the difference between primary production modified by burial and sulfate reduction modified by sulfide availability. As these rates converge, the potential consequences for P_{O2} increase.

1. Falkowski PG, Barber RT, Smetacek V (1998) Biogeochemical controls and feedbacks on ocean primary production. *Science* 281:200–206.
2. Hedges JI, Keil RG (1995). Sedimentary organic matter preservation—an assessment and speculative synthesis. *Mar Chem* 49:81–115.
3. Turchyn AV, Schrag DP (2006) Cenozoic evolution of the sulfur cycle: Insight from oxygen isotopes in marine sulfate. *Earth Planet Sci Lett* 241:763–779.
4. Canfield DE, Farquhar J (2009) Animal evolution, bioturbation, and the sulfate concentration of the oceans. *Proc Natl Acad Sci USA* 106:8123–8127.
5. Canfield DE, Thamdrup B, Kristensen E (2006) *Aquatic Geomicrobiology. Advances in Marine Biology*, vol 48 (Elsevier Academic, San Diego, CA).